

Semiannual Status Report
NASA Research Grant NsG-343, to the
University of Southern California
December 1, 1967

Submitted by R. Simha

FACILITY FORM 602

N68 - 13201	
(ACCESSION NUMBER)	(THRU)
5	1
(PAGES)	(CODE)
CR#91277	18
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

1. Multiple Transitions in Various Polymer Systems

We have obtained the thermal expansivities between about 20 and 120°K for ten of our polyalkyl methacrylates (PAMA) (studied earlier at liquid nitrogen temperatures), poly 4-methyl pentene-1 (P4MP1), a 49:51 ethylene-propylene copolymer (E-P), and several polyvinyl alkyl ethers (PVAE). The overlap between the liquid nitrogen ($T \geq 110^\circ\text{K}$) and helium data leads to maximum discrepancies of the order of 20% in the higher PAMA's and similarly for the PVAE's.

In PMMA the linear expansion coefficient α' is nearly constant ($20.1 \times 10^{-4}/^\circ\text{C}$) up to 60°K, increasing thereafter by a factor of 3 over an interval of 35° and centered around 83°K. No further relaxation region up to 200°K is evident. In the longer side chain methacrylates, on the other hand, α' increases monotonically up to 40°K, then remains approximately constant and is followed by a transition region between 80 and 110°K, depending on the polymer. Its magnitude increases with flexibility in the side chain. It would be interesting to see whether or not the above monotonic increase has its counterpart in PMMA. This would require measurements below 20°K. The plateau region is absent in the hexyl and octyl polymers, but, surprisingly, reappears in decyl. Here also $\Delta\alpha'$ is smaller than for the lower members of the series suggesting, as at higher temperatures, an effect due to side chain ordering. The existence of the transitions noted here is consistent with mechanical and proton spin relaxations observed by others.

P4MP1 behaves in a similar fashion as the PAMA, including the initial increase and a clear transition region centered at 88°K, but with a larger α' . In the E-P copolymer a transition appears at as low a temperature as 56°K, lower than we should have expected on the basis of the γ -transition in polyethylene.

The general pattern is similar for the C_2 to C_8 ethers investigated. The four ethers explored exhibit a relaxation region at 58 - 60°K and a further one around 95 to 105°K. We intend to examine this region further by means of dynamic

measurements. It is noteworthy to contrast the characteristic brittleness of these polymers with their ability to undergo transitions or relaxations, related to their side chains.

2. Equation of State Properties

The approach sketched in the June Report has been pursued. The equation of state obtained by combining a hard sphere model with an attractive term of a particular form and based on F \ddot{u} rth's theory does not lead to satisfactory results in the range of densities of interest here and does not presently encourage extension to chain liquids and polymers. Hence it is being discontinued.

We intend to revert to the free volume - hole theory described in earlier reports and the results obtained in collaboration with V. S. Nanda and Th. Somcynsky. The following aspects merit consideration: a) A comparison of the theory - experiment relationship for "true" monomer (rather than argon) versus polymer liquids. The series benzene, phenyl oligomers provides sufficient experimental data. Possibly some polyphenyl results suitable for our purposes are also available, or we may ourselves consider appropriate measurements in the future; b) A consideration of the Gibbs-diMarzio model, as modified by the ideas of Moacanin - Simha and of Eisenberg, incorporated properly into our equation of state treatment; c) A revision of our basic model to incorporate configurational properties of the polymer chain in deriving an equation of state. The pursuit of this program depends not only on technical matters but also on external circumstances in the coming year.

3. Publications

Multiple Transitions in Polyalkyl Methacrylates, R. A. Haldon and R. Simha, J. Appl. Phys., in press.

Transitions in Glasses at Low Temperatures, R. A. Haldon, W. J. Schell and R. Simha, J. Macromol. Sci., in press.

Thermal Expansivities of Polymers at Cryogenic Temperatures, in preparation.

4. Personal

R. A. Haldon completed a successful two years' postdoctoral stay in September and returned to Britain to join ICI's research laboratories in Pontypool.

After completing his stay at the Weizmann Institute as Kennedy Memorial Foundation Senior Fellow, R. Simha is spending the current semester on a British Research Council award at the Department of Chemistry, The University of Manchester, while on leave from USC. He is returning in February to join Case Western Reserve University.